Crystal and Molecular Structures of 2-Aminobenzophenone and 2-Aminodiphenylmethanol

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Crystals of 2-aminobenzophenone are monoclinic, space group $P2_1/c$, $a = 10.247(3)$, $b = 10.985(3)$, $c = 9.113(1)$ Å, $\beta = 99.03(1)°$, $Z = 4$. The structure was solved by direct methods and refined to $R = 0.042$ with 959 Mo-K_α diffractometer data. The molecular packing is due to intramolecular and intermolecular N–H···O hydrogen bonds, which determine a linear chain structure. Crystals of 2-aminodiphenylmethanol are rhombohedral, space group $R\bar{3}$, $a = 13.418(3)$ Å, $\alpha = 113.23(1)°$, $Z = 6$. The structure was solved by direct methods and refined with 916 observed reflections to $R = 0.064$. The molecules are linked into polymeric units by strong hydrogen bonds between the OH functions.

Benzophenone and its derivatives play an important role in organic chemistry, since they are intermediates in several syntheses of pharmaceuticals, such as benzodiazepines,[1] diazocines[2] and acetamides,[3] and in many photoreactions, including photo-Fries and the photo-Claisen rearrangements.[4] In physical organic chemistry they have made a substantial contribution to the development of photochemistry and electronic spectroscopy,[5] since they are very efficient triplet sensitizers in energy transport from their excited states to other species.[5–8] The radical character of triplet carbonyls is evident from their ability to abstract hydrogen from various hydrocarbon substrates.[9,10]

Benzophenones also present variable co-ordinating behaviour toward metal ions. In particular it has been observed that the introduction of another potential binding site, such as an amino group, modifies both roles of benzophenone as sensitizer[8] and its co-ordinating ability,[11] suggesting a correlation between these properties.

In view of our interest in the co-ordinating properties of these types of ligands, in order to learn more about their ligand behaviour, and to demonstrate any conformational change in passing from the free to the co-ordinated state, we have determined the crystal and molecular structures of 2-aminobenzophenone and its reduced form, 2-aminodiphenylmethanol.

Experimental

Preparation of Compounds.—2-Aminobenzophenone was supplied by Fluka and recrystallized from toluene or ethanol. 2-Aminodiphenylmethanol was prepared as reported in ref. 1 or by slow (one month) crystallization from an ethanol solution containing 2-aminobenzophenone and diphenylmercury.

X-Ray Data Collection.—All the *X*-ray measurements were carried out on an automated Siemens AED four-circle diffractometer, at room temperature, by using niobium-filtered Mo-K_α radiation ($\lambda = 0.710\,69$ Å). Lattice parameters were determined from least-squares refinements of θ values for 15 high-angle reflections accurately centred on the diffractometer.

Crystal data for 2-aminobenzophenone. $C_{13}H_{11}NO$, $M = 197.24$, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 10.247(3)$, $b = 10.985(3)$, $c = 9.113(1)$ Å, $\beta = 99.03(1)°$, $U = 1\,013.1$ Å^3, $D_m = 1.32$ (by flotation in CH_2Cl_2), $Z = 4$, $D_c = 1.293$, $F(000) = 416$, niobium-filtered Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 0.46 cm^{-1}, crystal dimensions *ca.* 0.72 × 0.72 × 0.13 mm.

Crystal data for 2-aminodiphenylmethanol. $C_{13}H_{13}NO$, $M = 199.26$, rhombohedral, space group $R\bar{3}$ (C^2_{3i}, no. 148), $a = 13.418(3)$ Å, $\alpha = 113.23(1)°$, $U = 1\,547.9$ Å^3, $D_m = 1.32$ (by flotation in CH_2Cl_2), $Z = 6$, $D_c = 1.282$, $F(000) = 636$, niobium-filtered Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 0.45 cm^{-1}, crystal dimensions *ca.* 0.38 × 0.26 × 0.24 mm.

For both crystals intensity data were collected with the ω–2θ scan technique in the θ 3—24° range, at a lowest scan speed of 2.5° min^{-1}. One standard reflection measured at 50 reflections intervals showed no significant changes during data collection. The intensities were corrected for Lorentz and polarization effects, but not for absorption in view of the negligible absorption coefficients. Of the 1 356 independent reflections measured for 2-aminobenzophenone 959 had $I \geqslant 3\,\sigma(I)$ and were used in subsequent calculations. A survey of the systematic absences allowed the space group $P2_1/c$ to be uniquely determined. A total of 1 801 reflections were measured for 2-aminodiphenylmethanol. Of these, 916 were significantly above background and were used in the structure analysis. Possible space groups, from absence of systematic extinctions, were $R3$, $R32$, $R3m$, and $R\bar{3}$, and $R\bar{3}m$. The space group $R\bar{3}$, initially assumed on the basis of intensity statistics and symmetry requirements, was confirmed by subsequent structure determination and refinement.

Solution and refinement of the structures. Both structures were solved by direct methods[12] and refined by full-matrix least-squares calculations,[12] with $\Sigma w(|F_0| - |F_c|)^2$ being minimized. 2-Aminobenzophenone was refined with anisotropic temperature factors on all non-hydrogen atoms, and with isotropic temperature factors on hydrogen atoms, previously located by ΔF maps. Convergence was reached at $R = 0.042$ and $R_w = 0.049$ $\{w = 1.0/[\sigma^2(F) + 0.0135\ F_0{}^2]\}$. The non-hydrogen atoms of 2-aminodiphenylmethanol were refined anisotropically, and in the last cycle only the positional parameters of the amine and hydroxy protons, located by previous ΔF maps, were allowed to vary; the remaining carbon-bonded hydrogen atoms were constrained to ride, with fixed temperature factors, at ideal positions (C–H = 1.08 Å) relative to the carbon atoms to which they are bonded. This model converged with $R = 0.064$ and $R_w = 0.076$ $\{w = 1.0/[\sigma^2(F) + 0.004\ F_0{}^2]\}$. During refinement, zero weight was assigned to one strong low-order reflection, which may be affected by secondary extinction. In both cases, the final Fourier difference maps were flat and featureless. Complex neutral-atom scattering factors[13] were used throughout; major calculation were carried out on a CDC Cyber 7600 computer, using the SHELX 76 system of

Table 1. Final fractional co-ordinates for 2-aminobenzophenone

Atom	*x*	*y*	*z*
C(1)	0.194 3(3)	0.497 3(2)	0.597 1(3)
C(2)	0.143 5(3)	0.607 6(2)	0.643 6(3)
N	0.046 7(2)	0.611 9(2)	0.729 9(3)
C(3)	0.197 7(3)	0.716 4(2)	0.601 6(3)
C(4)	0.289 7(3)	0.716 3(3)	0.508 8(3)
C(5)	0.336 5(3)	0.609 2(3)	0.456 7(4)
C(6)	0.289 6(3)	0.501 7(2)	0.501 6(3)
C(7)	0.145 9(3)	0.379 0(2)	0.639 4(3)
O	0.041 5(2)	0.367 2(2)	0.688 8(2)
C(8)	0.227 3(2)	0.268 3(2)	0.624 6(3)
C(9)	0.357 5(3)	0.259 0(3)	0.696 4(3)
C(10)	0.427 9(3)	0.152 3(3)	0.687 0(4)
C(11)	0.370 0(3)	0.056 2(3)	0.606 3(3)
C(12)	0.241 7(3)	0.064 5(3)	0.534 5(3)
C(13)	0.170 8(3)	0.169 4(3)	0.544 9(3)
H(1N)	0.005(4)	0.544(4)	0.740(5)
H(2N)	0.016(4)	0.691(4)	0.752(4)
H(3)	0.168(4)	0.798(4)	0.638(4)
H(4)	0.325(4)	0.786(4)	0.480(4)
H(5)	0.403(4)	0.606(3)	0.393(5)
H(6)	0.321(4)	0.426(4)	0.468(5)
H(9)	0.395(4)	0.332(4)	0.757(4)
H(10)	0.516(4)	0.144(3)	0.740(4)
H(11)	0.419(4)	−0.019(4)	0.592(5)
H(12)	0.201(4)	−0.005(4)	0.470(4)
H(13)	0.080(4)	0.177(4)	0.499(4)

Table 2. Final fractional co-ordinates for 2-aminodiphenylmethanol

Atom	*x*	*y*	*z*
C(1)	0.075 1(5)	0.905 4(5)	0.675 4(5)
C(2)	0.217 4(6)	0.988 4(7)	0.737 3(6)
N	0.306 2(6)	0.136 1(8)	0.826 8(7)
C(3)	0.271 6(9)	0.925 6(12)	0.710 0(9)
C(4)	0.189 6(12)	0.782 8(14)	0.626 7(10)
C(5)	0.052 4(9)	0.700 8(8)	0.570 4(7)
C(6)	−0.004 3(6)	0.763 2(6)	0.594 1(5)
C(7)	0.019 3(4)	0.977 7(4)	0.709 6(4)
O	0.072 6(3)	1.033 9(3)	0.848 8(3)
C(8)	−0.139 4(4)	0.884 4(4)	0.604 4(4)
C(9)	−0.202 5(5)	0.861 6(5)	0.480 2(4)
C(10)	−0.347 7(5)	0.781 2(5)	0.386 3(5)
C(11)	−0.429 5(5)	0.723 2(5)	0.415 1(5)
C(12)	−0.366 0(5)	0.746 0(5)	0.537 3(5)
C(13)	−0.222 1(5)	0.826 0(5)	0.631 9(5)
H(1N)	0.290(7)	1.187(6)	0.899(6)
H(2N)	0.413(6)	1.190(6)	0.893(6)
H(O)	0.047(5)	1.079(5)	0.882(5)

programs[12] and the ORTEP plotting program.[14] Final fractional co-ordinates of the refined atoms are given in Tables 1 and 2. Tables of atomic temperature factors and calculated hydrogen atom parameters are in the Supplementary Publication No. SUP 56096 (8 pp.).*

Results and Discussion

Description of the Structures.—Drawings of the structures, showing the labelling schemes, are given in Figures 1 and 2; diagrams of the molecular packing in Figures 3 and 4. Selected bond distances and angles are listed in Table 3. Lists of remaining bond distances and angles, and least-squares mean planes, are available as SUP 56096.

2-*Aminobenzophenone*. The dimensions of the molecule are similar to those found in its copper chloride[15] and mercury

Table 3. Selected interatomic distances (Å) and angles (°)

(A) Within 2-aminobenzophenone

C(2)–N	1.360(4)	C(7)–O	1.231(4)
C(7)–C(1)	1.464(4)	C(7)–C(8)	1.493(4)
N···O	2.713(3)	H(1N)···O	2.04(5)
N···O^{i}	3.073(3)	H(2N)···O^{i}	2.12(4)
N–C(2)–C(1)	122.7(2)	C(7)–C(8)–C(9)	121.6(2)
N–C(2)–C(3)	119.1(2)	C(7)–C(8)–C(13)	119.6(2)
C(7)–C(1)–C(2)	121.8(3)	C(1)–C(7)–O	122.6(2)
C(7)–C(1)–C(6)	119.3(2)	C(8)–C(7)–O	118.5(2)
C(1)–C(7)–C(8)	118.8(2)	N–H(1N)···O	133(4)
N–H(2N)···O^{i}	176(3)		

(B) Within 2-aminodiphenylmethanol

C(2)–N	1.386(8)	C(7)–O	1.407(5)
C(7)–C(1)	1.486(6)	C(7)–C(8)	1.491(5)
O···O^{ii}	2.699(5)	O–H(O)···O^{ii}	1.84(6)
N–C(2)–C(1)	121.1(5)	C(7)–C(8)–C(9)	119.3(4)
N–C(2)–C(3)	118.9(7)	C(7)–C(8)–C(13)	121.4(4)
C(7)–C(1)–C(2)	118.8(5)	C(1)–C(7)–O	105.9(3)
C(7)–C(1)–C(6)	122.6(4)	C(8)–C(7)–O	112.6(3)
C(1)–C(7)–C(8)	114.3(3)	O–H(O)···O^{ii}	172(5)

Superscripts refer to the following transformations of the reference co-ordinates: i, $-x, \frac{1}{2} + y, \frac{3}{2} - z$; ii, $1 - y, 2 - z, 1 - x$.

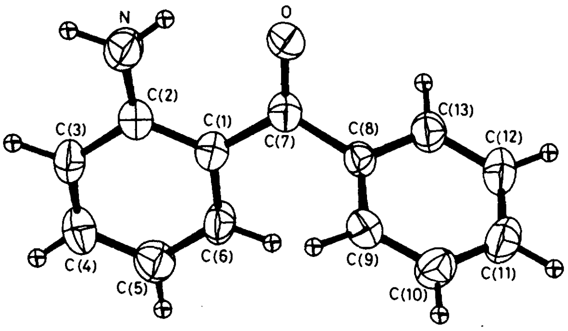

Figure 1. ORTEP view of 2-aminobenzophenone showing the atom numbering and thermal motion ellipsoids (50%) for non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

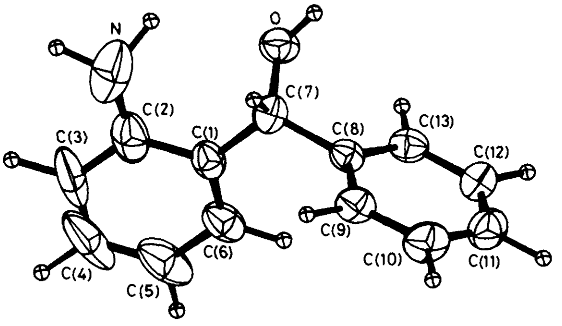

Figure 2. ORTEP view of 2-aminodiphenylmethanol showing the atom numbering and thermal motion ellipsoids (40%) for non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

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* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

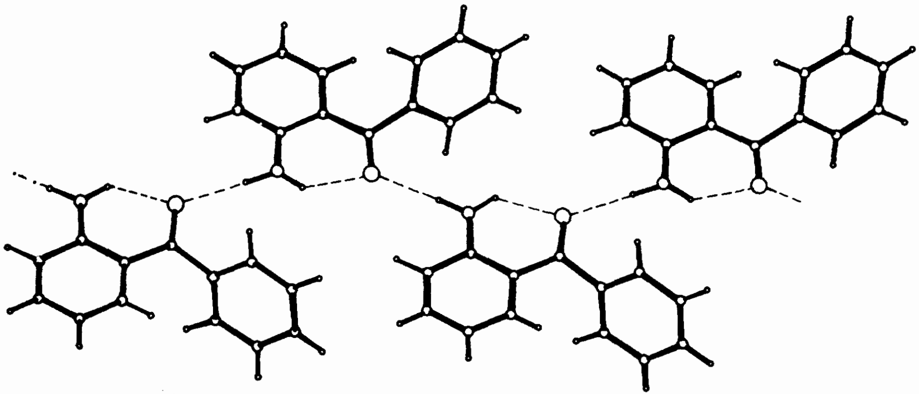

Figure 3. The molecular packing in 2-aminobenzophenone as viewed down the *c* cell axis. Broken lines represent hydrogen bonds

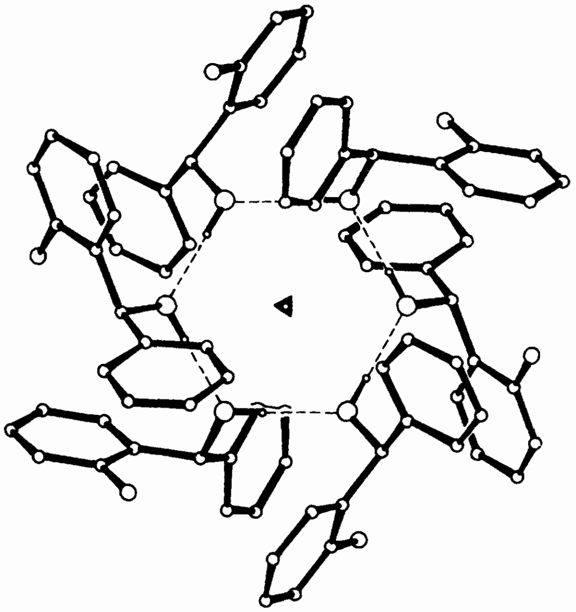

Figure 4. Arrangement of the 2-aminodiphenylmethanol molecules around $\bar{3}$. Broken lines represent hydrogen bonds. C- and N-bonded hydrogen atoms are omitted for clarity

bromide[11] adducts, and compare well with those observed in benzophenone[16,17] and its 4,4′-diamino derivative.[18] The C–N bond is notably shorter [1.360(4) than Å] in the metal complexes [1.443(5) and 1.39(3) Å for the Cu and Hg derivatives, respectively], in which the molecule acts as a nitrogen-donor ligand. The planes of the phenyl rings make dihedral angles of 19.1 and 56.1° with the planar carbonyl group, and are at 67.6° themselves; a similar twisted structure has been observed for all the benzophenone derivatives cited in refs. 15—18. It is interesting to note that the torsional motion of the substituted phenyl ring allows a strong intramolecular hydrogen-bonding interaction between one amine proton and the carbonyl oxygen (see Table 3), and that the same hydrogen bonding also occurs in the nitrogen-bonded metal adducts.[11,15] A further, intermolecular, hydrogen-bond interaction occurs between carbonyl oxygen and amine proton from an adjacent molecular unit; this interaction links the molecules into linear chains which parallel the *b* cell axis (see Figure 3). These chains are separated by normal van der Waals distances.

2-Aminodiphenylmethanol. Bond distances and angles are in the expected range; the somewhat short C–C bond lengths within the substituted phenyl ring [from 1.343(7) to 1.384(7) Å] were interpreted as due to the rather large thermal motion parameters of the involved atoms. The most interesting feature of the present structure is its molecular packing, resulting from hydrogen-bond interactions between hydroxy functions. Rather surprisingly, the amino group does not participate in any hydrogen-bond interaction, and this could account for the large thermal motion vibrations which affect the nitrogen and some adjacent carbon atoms. The strong, nearly linear, hydrogen bonds (see Table 3) between hydroxy functions link the molecules into polymeric units, which exhibit space-group symmetry (see Figure 4). In this case the phenyl rings are nearly perpendicular, with a dihedral angle of 87.9° between their mean planes. There are no short intermolecular contacts between units.

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